Catalytic dehydrogenation of hydrocarbon over iron-silicate ZSM-5

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Introduction
Zeolites containing trivalent metal element (Fe³⁺, Ga³⁺, B³⁺) other than Al³⁺ have been of interest in academy and industries. Different activity and selectivity has been reported for the zeolites substituted by trivalent metal elements even if the number of acid sites is not different for the samples with equivalent Si/Metal ratios. For example, the substitution of Al³⁺ for Fe³⁺ in ZSM-5 (Fe-ZSM-5) shows catalytic activity for olefin oligomerization but with less hydride-transfer reactions; it also shows higher selectivity for the acylation of propene. The acid sites in Al-containing zeolites are responsible for the catalytic activity of acid zeolites in hydrocarbon conversions. However, it is unknown if the typical protolytic chemistry, which is generally believed to be responsible for hydrocarbon conversions, is correct for Fe-ZSM-5.

Here, we present an investigation of the chemistry at the acid sites in Fe-ZSM-5 zeolites using the monomolecular propane reaction.

Materials and Methods
Aluminum free iron-silicate zeolites (Fe-ZSM-5) with two different Si/Fe ratios (40 and 80) are prepared using similar method reported by Bruckner. Iron(III) sulfate and sodium metasilicate are used for iron source and silica source, respectively. The sodium metasilicate dissolved in DI water is added to the solution of iron sulfate and sulfuric acid in DI water. TPABr is added to the resulted solution after good mixing. The amount of each material is calculated according to the desired Si/Fe ratios. The final mixture (pale yellow gel) is heated to 443 K for 3 days under rotation in Teflon-lined Parr autoclaves. Al-ZSM-5 with Si/Al ratio of 40 (Zeolyst CBV8014) is used as received. These materials are characterized by X-ray diffraction and N₂ adsorption isotherms.

The structure-activity relationship is investigated by using propane as a probe molecule. Propane conversion is performed in a plug flow reactor (ID = 4 mm). The sample is activated using this protocol: drying at 473 K and activation at 753 K under nitrogen flow. The products are analyzed by using GC with FID and TCD detectors. The products distributions for propane reaction are limited to the monomolecular reaction of propane in which H₂, propene, methane and ethene are produced. The formation of naphthalene radical cations is observed by using DRUVT spectroscopy. The sample is first activated at 753 K, and cooled down to room temperature, and then mixed with naphthalene under inert atmosphere.

Results and Discussion
Figure 1a shows the monomolecular propane reactions over H-Al-ZSM-5 and H-Fe-ZSM-5. H-Al-ZSM-5 shows both cracking and dehydrogenation. In contrast, dehydrogenation is the main reaction channel for the propane conversion over H-Fe-ZSM-5. The amount of products formed via cracking pathway (methane and ethane) is too small to quantify. In addition, H-Fe-ZSM-5 shows higher reaction rates than H-Al-ZSM-5 with the same Si/M ratio for the propane conversion. The activation energy for dehydrogenation over H-Fe-ZSM-5 (114 kJ/mol) is lower than those of H-Al-ZSM-5 (180 ~ 204 kJ/mol)⁵, suggesting a different chemistry can work at the acid sites in H-Fe-ZSM-5. In a previous report, it was shown that naphthalene radical cations form on the dehydroxylated samples of H-Al-ZSM-5 but not on the dehydrated samples indicating that redox sites have formed. The formation of naphthalene radical cations is also observed for the activated H-Fe-ZSM-5 at 723 K (Figure 1b; there is no formation of naphthalene radical cations for H-Al-ZSM-5), suggesting the redox chemistry is potentially responsible for the catalytic activity in H-Fe-ZSM-5.

Significance
Surprisingly, very high selectivity toward dehydrogenation is observed for the propane conversion over H-Fe-ZSM-5. This work can provide evidence for different catalytic chemistry in H-Fe-ZSM-5 other than typical protolytic chemistry.

References